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STRONG AND WEAK MAGNETIC COUPLING IN CHROMIUM

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Strong and weak magnetic coupling in chromium

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Utilizing *ab initio* molecular dynamics and quantum Monte Carlo simulations we calculate an extensive set of thermodynamic quantities for chromium. Employing an effective magnetic model allows us to investigate two different scenarios: A weak magnetic coupling scenario for Cr, as intuitively expected from the Néel temperature of 311 K, turns out to be in clear disagreement with experimental observations. The discrepancies indicate that a weak magnetic coupling is unlikely to be the dominant source of magnetic entropy. Assuming a strong magnetic coupling scenario for Cr atoms provides within our approach the only possible solution for which a consistent picture with very good agreement to experimental data emerges. This finding is consistent with a hierarchy of energy scales in chromium as recently found by Jaramillo *et al.* [Nature **459**, 405 (2009)].

I. INTRODUCTION

Chromium is a key material in many practical applications and, in particular, a decisive ingredient for stainless steels.[1–3] At low temperatures it is commonly accepted that bcc Cr displays antiferromagnetic order in form of an incommensurate spin density wave (SDW) modulated by a wave vector Q. The SDW is accompanied by a second-harmonic charge-density wave (CDW) modulated by $2Q$.[4,5] A spin-flip transition is observed at around 123 K at which the polarization of the spin wave changes from transversal to longitudinal, i.e., spin alignment is shifting from perpendicular to parallel with respect to Q. Confusion persisted for some time about the exact location of the Néel temperature $T_{\text{Néel}}$ and the origin of certain anomalies close to $T_{\text{Néel}}$. Most theoretical and experimental work focused therefore on resolving this issue.[4] Today, the debate has been settled with the peculiar dependencies attributed to experimentally difficult-to-control Cr_2O_3 impurities and with $T_{\text{Néel}}$ being fixed rather accurately down to 311 K.

While the low temperature range is well understood, anomalies at high temperatures are posing so far unanswered questions. Various measurements conducted over the last thirty years have revealed peculiarities in the expansion, its coefficient, heat capacity and elastic moduli well above $T_{\text{Néel}}$ (see Ref. [6] and references therein). White and Andrikidis[6] showed for instance that the increase in the linear expansion coefficient strongly exceeds even the ones of Mo and W, which themselves are known to have high coefficients due to anharmonic contributions. These results were affirmed by Dubrovinskaia *et al.* by *in situ* X-ray diffractometry.[7] It was speculated[6] that anharmonic or magnetic contributions are responsible for the strong increase in the thermodynamic data. Indications for a large magnetic contribution were provided by Grimvall *et al.*[8] who used an empirical model to derive the magnetic entropy of Cr. The resulting temperature dependence of the empirical magnetic entropy shows a remarkable increase between 1000 K and the melting temperature (see solid black line in Fig. 1). Arguments relating the findings to a hierarchy of energy scales were provided[9,10] but it becomes clear that a concrete and complete picture of the excitation mechanisms in Cr is missing so far.

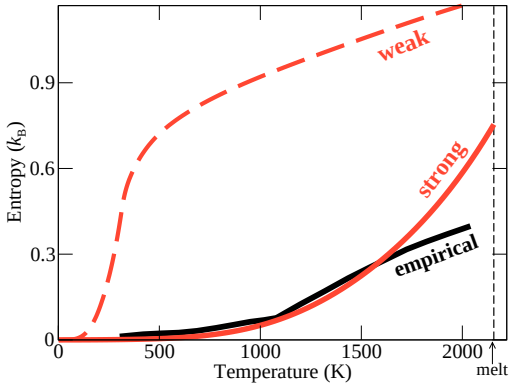

FIG. 1: (Color online) Magnetic entropy of bcc Cr in units of the Boltzmann constant k_B. The dashed (solid) red curve corresponds to a calculation based on weak (strong) magnetic coupling. The solid black line is an earlier empirical assessment of Grimvall *et al.*[8] and the vertical dashed line indicates the melting point (2156 K).

In this report we provide first-principles calculations showing that a possible solution to the high temperature anomalies are strong magnetic fluctuations. The results are in agreement with recent experimental indications of pseudo-gap formation and the coexistence of a weakly coupled ground state and high-energy excitations. Our arguments are based on an integrated and state-of-the-art first-principles technique, which we have developed previously. Our treatment of lattice vibrations accurately accounts for effects beyond the simple quasiharmonic picture by utilizing *ab initio* molecular dynamic simulations with additional speed-up algorithms.[11,12] This allows us to systematically clarify the role of anharmonic contributions on a quantitative level as opposed to previous empirical estimations. To capture the magnetic con-

tributions we utilize an effective Heisenberg model[13–17] with spin-fluctations implicitly taken into account via self-consistently determined volume-dependent magnetic moments. The presence of a single effective magnetic exchange parameter allows us to investigate and to differentiate between possible magnetic scenarios. Such an effective Heisenberg approach has been proven to perform excellently for a wide range of ferromagnets such as Fe,[15] Co,[15] Fe_3C[16,17] or even weakly localized (more itinerant) systems such as Ni,[15] provided that the experimental magnetic transition temperature is adjusted.

II. TECHNICAL DETAILS

The DFT calculations in the following are performed using the VASP[18] package employing the projector augmented wave (PAW) method[19] within the generalized gradient approximation (Perdew-Burke-Ernzerhof parametrization[20]). Phonon calculations for obtaining the quasiharmonic free energy are done in supercells with up to 128 atoms. Up to 30,000 **k**-points times atom and a plane-wave cutoff energy of $E_{\rm cut} = 340$ eV are chosen for up to 7 volumes to ensure converged vibrational free energy contributions ($<$ 1 meV per atom) in the considered temperature range (up to 2156 K). Anharmonic calculations are performed in a 54 atomic supercell and for the non-magnetic state. We use the UP-TILD method[11] with a 2×2×2 **k**-point mesh and $E_{\rm cut} = 210$ eV as low converged parameters and a 6×6×6 **k**-point mesh and $E_{\rm cut} = 270$ eV as high converged parameters. Explicit checks show that these values give an error of $\approx$ 1 meV/atom in the free energy. We use a time step of 5 fs and a friction parameter of 0.01 for the Langevin dynamics. For each volume, temperature, and coupling parameter λ, we follow the molecular dynamics for 5000 steps (25 ps) after equilibration. For each temperature and volume, we sample a mesh of six coupling parameters (λ =0, 0.2, 0.4, 0.6, 0.8, 1) and use the proposed cotangent fit[12] for parameterization. We use a dense mesh of >30 volume-temperature points (7 volumes in the relevant range at 1000 K, 1500 K, 2000 K and 3 volumes at 500 K, 750 K, 1250 K, 1750 K) as fitting input to the parameterization based on a renormalized average frequency[11], $\omega^{\rm ah} = a_0 + a_1 T + a_2 V + a_3 TV$, with $a_0 \dots a_3$ fitting coefficients. Statistical errors in the anharmonic free energy are well below 1 meV/atom. For the electronic contribution a parametrization of the (T, V)-dependence on a grid including 10 T-steps and 10 volumes employing $\approx 130,000$ **k**-points times atom provides converged electronic free energy contributions.

The effective Heisenberg model is solved employing QMC calculations with the direct-loop algorithm in the stochastic series expansion as implemented in the ALPS code.[21] Monte Carlo calculations involve 2.5×10^6 steps including thermalization and statistical averaging. The model calculations are carried out for supercells containing $\approx$ 6000 atoms. The effective spins S entering the Heisenberg model contain the volume dependence of the calculated ground state local magnetic moments $M(V) \approx 2\mu_B S$. The exact solutions for $S_1 \le S \le S_2$ ($S_2 - S_1 = 1/2$) are computed and an interpolation $F^{\rm mag}(T,S) = \rho F^{\rm mag}(T,S_2) + (1-\rho)F^{\rm mag}(T,S_1)$ is employed afterwards to obtain the magnetic free energy $F^{\rm mag}$. $\rho(S) = \frac{S^{\rm mag}(S)-S^{\rm mag}(S_1)}{S^{\rm mag}(S_2)-S^{\rm mag}(S_1)}$ is chosen to fulfill the high temperature limit for the magnetic free energy provided by the entropy limit $S^{\rm mag} = \log(2S+1)$ of fully disordered spins.

III. RESULTS

Following previous successful studies,[15–17] we start with an obvious but—as it will turn out—too naive scenario: According to the experimental Néel temperature, we parametrize our Heisenberg Hamiltonian by tuning the exchange interaction to reproduce $T_{\rm Néel}$=311 K. We know from our previous studies that a subsequent solution using quantum Monte Carlo gives us not only a correct description of the quantum mechanical nature of the Heisenberg model at low temperatures, but also an accurate account of the paramagnetic state of the model beyond the magnetic transition temperature including short-range order. In addition, we compute electronic, quasiharmonic, and anharmonic excitations of chromium and obtain therefore the complete free energy surface over the full temperature range. The resulting thermodynamic properties are shown by the dashed lines in Fig. 2 and compared to experimental data denoted by black symbols.

The comparison with experiment is unambiguous: All properties based on an effective Heisenberg model with weak magnetic coupling show consistently huge discrepancies with experimental data. One particularly important observation is that the discrepancies are not only found for the high temperature window, in which the experimental scatter for some physical properties might blur the comparison, but also for low temperatures (<200 K). For low temperatures experiment is conclusive (little scatter) and in addition *ab initio* can be in general expected to yield accurate results for thermodynamic properties.[47] However, from Fig. 2 we learn that this expectation breaks down for Cr if a weak magnetic coupling is assumed and that, for instance, the expansion coefficient is off by more than a factor of two already at 200 K.

The origin of the failure can be traced back to the temperature dependence of the magnetic entropy shown in Fig. 1 by the dashed line. By assuming weak magnetic coupling, the magnetic degrees of freedom acquire very rapidly a large amount of entropy already at low temperatures before reaching $T_{\rm Néel}$. Above $T_{\rm Néel}$, the magnetic entropy quickly converges to the limit of fully disordered spins $-k_{\rm B}T\ln(M(V)+1)$, with temperature T, volume V, and with the volume-dependent local magnetic moment $M(V)$. Driven by the large amount of entropy, the bulk

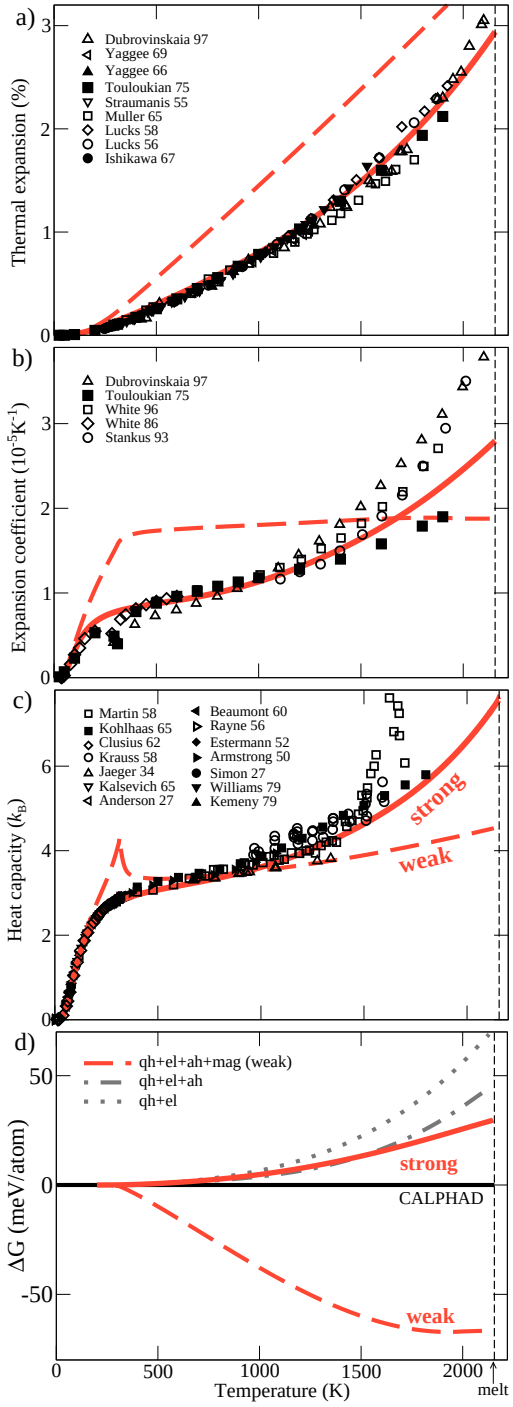

FIG. 2: (Color online) Temperature dependence of thermodynamic properties for bcc Cr: a) linear expansion, b) linear expansion coefficient, c) heat capacity, and d) Gibbs energy. Black symbols are experimental values from various measurements[6,22–46] and red lines show our theoretical results. The dashed (solid) line corresponds to the weak (strong) coupling scenario. Vertical dashed lines indicate the melting point (2156 K). The Gibbs energy in d) is referenced with respect to values obtained from the CALPHAD approach (SGTE unary database) and additionally the dependence of the quasiharmonic plus electronic (qh+el) contribution and the one of the quasiharmonic plus electronic plus anharmonic (qh+el+ah) contribution is shown.

rapidly expands due to the increase of M with increasing V, much stronger than the experimentally observed thermal expansion and its coefficient (Fig. 2 (a) and (b)). The steep increase in magnetic entropy is also responsible for the pronounced peak in the heat capacity at 311 K (Fig. 2 (c)). A peak at this temperature is observed in the experimental heat capacities as well,[4] but orders of magnitude smaller (therefore not visible in Fig. 2c) than the *ab initio* result based on $T_{\text{Néel}}$=311 K.

One may argue that—although our model accounts *implicitly* for longitudinal spin-fluctuations—*explicit* longitudinal spin-fluctuations could change the result. This argument can be, however, ruled out by considering that an additional degree-of-freedom will lead to an even faster increase in magnetic entropy resulting in yet larger discrepancies. We are therefore apparently stuck in a dilemma with large discrepancies between intuitive theory and experiment.

In view of the failure of a weak coupling scenario the question arises whether there is a physical basis supporting a strong magnetic coupling. Indeed, a detailed literature analysis clearly indicates that this is a viable possibility. As mentioned above the SDW in Cr is intrinsically coupled to a CDW.[5] Based on the involved electron-hole pseudo gaps high energy excitations on an energy scale of $\approx 5k_{\text{B}}T_{\text{Néel}}$ are present in Cr as experimentally shown by optical measurements.[48] The intrinsic coupling between the charge and spin density waves can result in strong magnetic fluctuations, a relation which has been recently pointed out by Jaramillo and co-workers.[9,10] In Ref. [9] an estimate of the magnetic exchange interaction of 140 meV is provided, which is much larger than one would expect from $T_{\text{Néel}}$=311 K (26.8 meV). In fact, there are several experimental studies addressing the magnetic degrees-of-freedom directly and a general conclusion seems to be that Cr exhibits strong magnetic coupling effects: For example, spin wave excitations with energies up to 400 meV (Ref. [49]) and spin wave velocities up to 1.5×10^5m/s (Ref. [50]) were found in $Cr_{0.95}V_{0.05}$ samples. These unusually high values are an indication of rather strong effective magnetic exchange interactions at high temperatures. Further evidence is provided by several other studies: 1) strong effective magnetic exchange interactions recently found in Ref. [9]. 2) Neutron scattering experiments suggesting strong magnetic interactions at least up 600 K.[4] 3) Magnetic correlations extending over 11 bcc unit cells even up to 700 K.[51] 4) Absorption peaks in the infrared spectra of Cr and Cr alloys with a maximum around $\approx$ 1590 K.[52] All these studies conclude that strong magnetic correlations are present at high temperatures, much higher than $T_{\text{Néel}}$ at which the long-range-ordered SDW disappears. This clearly indicates that the phase above the Néel temperature remains a highly correlated regime and that the system did not yet reach its completely disordered magnetic state.

Some experimental works even provide indications for a high temperature magnetic transition: 1) Krauss *et al.* performed specific heat capacity measurements which

show a maximum in the range 1600-1700 K.[31] 2) Similar observation were found by Grube and Knabe in electric resistivity measurements, where an anomaly is observed in a slightly higher temperature range of 1813-1853 K.[53] 3) Another indication for a high temperature magnetic transition was given by magnetic susceptibility measurements by McGuire and Kriessman, who reported a transition about $\approx$ 1673 K.[54]

To comply with these observations we make the following attempt: We mimic the observed strong magnetic fluctuations by assuming considerably stronger spin interactions in our magnetic model. It is an advantage of our effective model that a corresponding calculation can be nicely and computationally easily integrated by a renormalization of the interaction parameter within the Heisenberg Hamiltonian. The remaining calculations have been performed as in the low $T_{\text{Néel}}$ case by solving the Hamiltonian with quantum Monte Carlo and adding the (same) quasiharmonic, electronic, and anharmonic contributions to the resulting free energy. As for the specific value of the Néel temperature we fix it to a considerably higher value. In order not to introduce additional arbitrariness we choose the melting temperature of 2156 K. The dependencies for the resulting thermodynamic quantities are shown by the solid red lines in Fig. 2.

The comparison of the *strong* coupling results with experiment turns out to be in striking contrast to the *weak* coupling comparison. The agreement with experiment is now consistently good over the whole temperature range for all quantities. This consistent description of materials properties is remarkable keeping in mind that the different properties explore rather different paths and derivatives on the complex free energy surface. As for the low $T_{\text{Néel}}$ case, we can again trace back the dependence of the thermodynamic properties to the temperature dependence of the magnetic entropy (solid red line in Fig. 1). The steep increase we have observed for the low $T_{\text{Néel}}$ curve (dashed line) at low temperatures is now strongly suppressed and the magnetic entropy becomes significant only above 1000 K. This is in very nice agreement with the empirically derived magnetic entropy.[8]

The striking contrast between the weakly coupled ground state and strong fluctuations was discussed recently by Jaramillo *et al.*[9,10] The key is to realize that the magnetic system in Cr exhibits two distinct energy scales. The experimentally verified[9] BCS-type ground state exhibits quasi particle excitation gaps in the order of $5.1 k_{\text{B}} T_{\text{Néel}} \approx$ 1590 K. These pseudo particles are responsible for the strong spin correlations observed at high temperatures. This is the reason why even well above 311 K, significant magnetic order is found in experiment.[51] We note that these strong magnetic contributions may not be observable by standard DFT since they are likely a result of the delicate interplay between SDW and CDW involving strong electronic correlations. Studies going beyond standard DFT (e.g., LDA+U, dynamical mean field theory, GW) will allow further insight, but are beyond the scope of the present manuscript.

In addition our effective magnetic model can by construction not account for the spin-flip transition around 123 K as well as for the disappearance of a long-range incommensurate spiral state at 311 K. This is the reason why the dip at 311 K observed in the experimental expansion coefficient is missing in our calculations. Further, we expect that our data, in particular for the high temperature region of the expansion coefficient and the heat capacity, might be modified (tentatively: increased) by an additional coupling between the magnetic and vibrational system[55] and by the occurrence of vacancies. Those effects, not considered in our study, will provide however only quantitative changes, while leaving the qualitative results untouched.

IV. CONCLUSION

In conclusion, the Néel temperature of 311 K in Cr is apparently a manifestation of the disappearance of *long-range* (incommensurate) spin states. The temperature at which one can expect a *magnetically fully disordered* state is considerably higher as our *ab initio* calculations show. Furthermore, anharmonic contributions beyond the quasi harmonic approximation are not the dominant source for the unusual thermodynamic behavior at higher temperatures. Good agreement with experiment up to the melting point demonstrates that the major magnetic and thermodynamics effects of bcc Cr can be accurately captured with an effective Heisenberg Hamiltonian with strong magnetic coupling.

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